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(54) Title: ACID TREATMENT FOR DECAFFEINATION OF COFFEE

(57) Abstract

A method for producing decaffeinated green coffee beans includes a step of contacting the beans with an acidic fluid and step of decaffeinating the acidified beans by supercritical extraction. The acidic fluid is desirably an aqueous solution of an acid normally present in green coffee beans or roast coffee beans, preferably citric acid. The acidifying treatment compensates for loss of acidity which occurs during supercritical decaffeination which adversely affects the flavor and aroma of coffee beverage.

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ACID TREATMENT FOR DECAFFEINATION OF COFFEE

Background of the Invention

This invention relates to decaffeination of green coffee beans. More particularly, this invention relates to treatment of green coffee beans prior to or simultaneously with decaffeination. Still more particularly, this invention relates to treatment of green coffee beans by contacting them with an aqueous organic acid solution in connection with supercritical extraction of caffeine.

Many processes are known for decaffeination of coffee. One particularly preferred process is supercritical extraction of caffeine, typically performed using supercritical carbon dioxide, perhaps with cosolvents such as water or so-called enhancers. Such processes are disclosed, for instance, in U.S. Patent Nos. 4,820,537 and 4,260,639. Such processes practiced to the present have suffered in their ability to produce coffee comparable in flavor and aroma to non-decaffeinated coffee.

While supercritical carbon dioxide is an effective decaffeination medium, its solvent action is not specific to caffeine or caffeine precursors. During supercritical decaffeination of green coffee beans, numerous other components are removed including but not limited to waxes, oils, and color bodies. Applicants have discovered that water soluble components including acidic species are also removed from the green coffee beans. It is known that the pH of a coffee beverage contributes to perceived flavor, and that the range of pH for acceptable palatability is from about 4.95 to about 5.15. Others have attempted to control the pH of final coffee product, i.e., instant or roast and ground coffee, by adding acidic or alkaline substances t th final

coffee product to account for unacceptable pH caused by such factors as the botany of th coffee beans, the altitude at which th y are grown, th processing method applied to the coffee fruit, the age of the beans when processed, and the degree of roasting. See, e.g., Sivetz, *How Acidity Affects Coffee Flavor*, Food Technology, Vol. 25, No. 5, 1971, pages 70-77. However, there appears to be no recognition in the art that supercritical decaffeination adversely affects acidity, nor does there appear to be any method disclosed for controlling the acidity of coffee products other than final coffee products.

Summary of the Invention

It is therefore an object of the invention to provide a method of decaffeinating green coffee beans without adversely affecting their acidity or the flavor of coffee beverages produced from them. It is a further object of the invention to provide such a method useful with supercritical decaffeination, in particular with caffeine extraction using supercritical carbon dioxide. In accordance with the invention, green coffee beans are subjected to a treatment by contacting them with an acidic fluid, preferably an aqueous citric acid solution, prior to or simultaneously with decaffeination. These and other objects and features of the invention will become apparent upon review of the following specifications and appended claims.

Detailed Descriptions of the Preferred Embodiment

The process of the invention comprises treatment of green coffee beans with an acidic fluid which is capable of being absorbed by the green coffee beans, to provide acidified green coffee beans. The acidified green coffee beans are subjected to decaffeination, preferably by supercritical fluid extraction. In the acidifying step green coffee beans are contacted with an acidic fluid, pref rably an aqu ous

acid soluti n. It is believed that any acidic fluid will be eff ctiv in the method of th invention (albeit with possible drawbacks such as cost or toxicity) so long as it produces upon absorption green coffee beans which are acidified to the degree necessary so that, after decaffeination, an appropriate acidity is achieved such that the final coffee product will produce coffee beverage having an acceptable "brightness" or acidic character to its flavor. However, it is believed preferable to use an aqueous organic acid solution, and particularly preferable to use an aqueous solution of an organic acid which is naturally or normally present in green coffee beans or roast coffee beans. Such acids include volatile acids such as acetic, propionic, butyric, valeric, caffeic, and quinic, which are produced during roasting, and nonvolatile acids such as chlorogenic, tartaric, citric, malic and oxalic which are naturally present in green coffee beans. Of the foregoing, chlorogenic, tartaric, citric, and malic acids are preferred; oxalic acid is less preferred because it has some toxicity to humans. Because the citric acid is highly dissociated in aqueous solution, and because it may be easily and inexpensively obtained in food grades, it is particularly preferred.

The acid treatment is carried out using conditions of time, temperature, and acid concentration to achieve the desired acidification of the green coffee beans in view of their natural characteristics and the further processing methods to be employed.

Acid treatment of green coffee beans may be carried out as a pretreatment step prior to decaffeination, where it may be easily controlled and where it may be combined with a moisturizing step typically performed prior to decaffeination. Acid treatment of the green coffee beans may also be combined

and performed simultaneously with the decaffeination step.

Since green coffee beans are frequently moisturized by contacting them with water or steam prior to supercritical decaffeination, typically to a moisture content above 20% and usually about 25% to about 50%, the acidifying pretreatment step of the invention is desirably performed during such moisturizing. Accordingly, the pretreatment step is desirably carried out so that when the desired moisture content has been achieved, the desired acidification of the green coffee beans has also been achieved.

After the acidification step, the acidified moist green coffee beans are subjected to decaffeination, preferably by supercritical extraction. The supercritical extraction step may be performed using known processes, including known supercritical fluids, cosolvents, pressures, temperatures, and times. Extraction using supercritical carbon dioxide is especially preferred, since carbon dioxide is relatively inexpensive, effective, and does not leave any toxic residues in the decaffeinated beans. Such supercritical extraction may be accomplished using conventional extraction and separation vessels.

Both the acid treatment step and the supercritical extraction step of the invention may be performed in a batch, continuous, or pseudo-continuous process.

Example

5 pounds of green coffee beans, having a caffeine content of about 1.12% by weight, were steamed for about 15 minutes and loaded into a wetting device which recirculated 3.4 pounds of a 2.0% by weight citric acid/water solution. The wetting device was designed so that the citric acid solution was fed to a spray head and sprayed over the beans, percolat d through them,

collected at the bottom, and then pumped back to the spray head. This was performed at about 60°C. - 80°C. until the solution had been entirely absorbed into the beans, approximately 45 minutes. The resulting beans had a moisture content of about 30.6%.

The pretreated green coffee beans were loaded into a basked which was placed inside a supercritical extraction vessel containing 5 pounds of water in the bottom of the extractor. The beans were suspended about 12 inches above the water level. The extractor was sealed and purged for 5 minutes with carbon dioxide to eliminate any air. The extractor and its associated separator were then brought up to process conditions, namely and extractor temperature of 90°C., an extractor pressure of 280 bar, a separator temperature of 30°C. - 40°C., and a separator pressure of 70 - 80 bar. The extractor charge was subjected to supercritical carbon dioxide with a flow rate of 141 pounds of carbon dioxide per hour for an 8 hour period. During the extraction process, a cosolvent pump was operated at a rate to maintain the water content of the system within ½ pound of its initial value. At the end of the 8 hour supercritical extraction run, the system was slowly depressurized through the separator. The beans were removed from the extracted and dried to a moisture content of about 7% - 10%.

Beans treated with the process of the example were analyzed and tested by high performance liquid chromatographic methods which revealed a final caffeine content of 0.043% by weight, which corresponds to a decaffeination level of 96.2%.

Coffee produced by the method of this example and coffee produced by substantially the same method but without acidic treatment were subjected to evaluation and flavor analysis according to standard techniques. These include preliminary examination of the green coffee beans

for color. The beans are then roasted and ground, and the product again evaluated for color. The roast and ground coffee is then brewed by adding boiling water and allowing it to steep. Brewed coffee is then evaluated for flavor, color, and aroma by three trained and qualified tasters according to a standard scale containing 13 gradations, including A (best), B9-B5, C8-C4, D3-D2, and F. The scores provided by the individual tasters are averaged, to produced averaged scores.

Coffees produced according to the method of this example were scored as C8 and B-5 (acceptable) in several tests. Coffees produced substantially to the method of the example, but without acidic treatment, were scored C-4 (bad).

Any acidification will be of some benefit with green coffee beans which produce excessively alkaline coffee upon decaffeination and further processing to coffee beverage. However, applicants' tests suggest that with typical coffees of the arabica variety using citric acid pretreatment in the manner of the above example, acid concentrations in the range of about 0.05% to about 3.5% by weight are preferred, that citric acid concentrations in the range of about 1.0% to about 3.0% by weight are more preferred, and that a citric acid concentration of about 1.5% to about 2.0% is most preferred.

The acid pretreatment process is conveniently carried out at room temperature, however, it will be understood that other temperatures, desirably between about room temperature and about 80°C., may be used. It will also be understood that the desirable degree of acidification will depend on the nature of the green coffee beans to be decaffeinated as well as on the decaffeination process and the process used to convert the acidified decaffeinated coffee beans to final coffee product.

Th degree of acidification may be controlled by the selecti n of th particular acid used, and the time during which and temperature at which the beans are contacted by the acid solution.

In the nature of the example above, applicants have found it preferable to contact the green coffee beans with an aqueous organic acid solution of sufficient solution to beans ratio and sufficient acid concentration that when the solution is fully absorbed into the beans, the beans have reached the desired moisture content and desired degree of acidification. The desired moisture content by weight is preferably above about 20%, more preferably between about 25% and about 50%, and most preferably between about 30% and about 35%. With the preferred acid solution, aqueous citric acid solution, and with pretreatment of the beans to achieve a moisture content of about 30% to 35%, the solution is preferably between about 0.5% and about 3.5%, and more preferably between about 1.0% and 3.0%, most preferably about 1.5% and about 2.0% citric acid by weight. If other acids are used, their concentration in the solution may be adjusted so that the hydrogen ion concentration in the pretreatment solution is equivalent to that of the citric acid solutions specified above, whereby solutions which are equivalent to their acidification of the beans may be obtained.

While control of the pretreatment process is easiest when a batch process is used with fixed initial quantities of solution and beans and the treatment is carried out until the solution is fully absorbed, or in a batch or continuous process wherein quantities of solution in excess of the amount which may be absorbed into the beans are used and the process is carried out until the acid concentration in the beans is the same as th acid concentration in the solution, it will be understood that ther m thods may be used. F r instance,

acid solution of higher hydrogen ion concentration than the citric acid solutions specified above may be used, and the pretreatment process conducted for a time shorter than that necessary to reach equilibrium. Such methods may, however, require other steps to achieve desired moisture content.

As indicated above, green coffee beans are often steamed prior to decaffeination. In addition to moisturizing the beans, the steaming step swells beans to a greater extent than moisturizing by soaking, and thus makes subsequent caffeine extraction easier. Applicant has found it advantageous to both steam and soak the beans, preferably simultaneously. Accordingly, in a preferred embodiment of the invention, the beans are subjected to pretreatment comprising simultaneously subjecting them to a flow of steam and contacting them with an acidic fluid. This may be accomplished by loading a vessel with a change of beans, supplying steam to an inlet near the bottom of the vessel, withdrawing steam from an outlet near the top of the vessel, and spraying acidic fluid such as aqueous citric acid solution over the beans from a spray head near the top of the vessel. Acidic fluid collecting in the bottom of the vessel after passing over the beans may be recirculated to the spray head.

As indicated, decaffeination of the pretreated acidified green coffee beans is preferably accomplished by a supercritical extraction step using supercritical carbon dioxide, most preferably using moist carbon dioxide, i.e., using water as a cosolvent. Applicants believe that the extraction step is preferably carried out at a pressure in excess of 200 bar, more preferably at a pressure in excess of about 240 bar, and most preferably at a pressure between about 250 bar and about 310 bar. Applicants further believe that the extraction step is preferably carried out at a temperature above the

critical temperature, more preferably at a temperature between about 60°C. and about 120°C., and most preferably at a temperature between about 70°C. and about 110°C. The extraction is preferably carried out with a solvent/feed ratio of between about 50/1 and 300/1, and most preferably between about 75/1 and about 275/1. Applicants believe, however, that the specified extraction parameters are desirable primarily because of ease and effectiveness of the extraction step itself, rather than because of a relationship with the acidifying pretreatment step.

In a particularly preferred decaffeination process, the green coffee beans are subjected to moist supercritical carbon dioxide as described above, wherein the supercritical fluid is passed through an acidic fluid prior to contacting the beans. For instance, a volume of acidic fluid such as aqueous citric acid may be maintained in the bottom of the extraction vessel. Supercritical carbon dioxide may be introduced into the bottom of the vessel, whereupon it bubbles through the citric acid solution, entraining citric acid as well as water. This process tends to maintain the citric acid balance, by reducing dissolving of the citric acid which was introduced into the beans during pretreatment.

In view of the foregoing, it will be understood that the acidification of green coffee beans may be combined with the decaffeination step. Thus, green coffee beans may be introduced into an extraction vessel and decaffeination in the presence of an acidic fluid. For instance, pretreatment of green coffee beans may be dispensed with and they may, after any desired steaming step or the like, be introduced into a supercritical extraction vessel having a volume of acidic fluid such as aqueous citric acid in the bottom. Supercritical carbon dioxide may be introduced at the bottom of the vessel, where it will bubble through an entrain th acidic fluid.

The green coffee beans will then become acidified by absorbing acidic fluid while caffeine is extracted by the supercritical fluid.

Decaffeination of coffee is desirably preferred until at least about 90%, and more preferably at least about 97%, by weight of the caffeine content is removed. Since green coffee beans typically contain from about 0.6% to about 3.0% caffeine by weight, the decaffeination process in accordance with the present invention is preferably carried out until the caffeine content of the beans is less than about 0.3% by weight, and more preferably until the caffeine content is less than about 0.1% by weight.

Supercritical carbon dioxide is the preferred process for decaffeination used in the present invention. It is also the process which, to the applicants' knowledge, is the most selective, i.e. most effective in removing caffeine but not other compounds from the green coffee beans. Accordingly, it is believed that the acidic treatment of the present invention will also be beneficial in connection with decaffeination using other processes which remove substantial amounts of non-caffeine compounds from green coffee beans. Such other known decaffeination processes include the methylene chloride process, the ethyl acetate process, the water-based process, and the process known as the "Nestle™" or coffee oil process. Moreover, it is believed that such other decaffeination processes may lend themselves to simultaneous acidification and decaffeination. For instance, in a modified water-based process, the green coffee beans may be acidified during decaffeination by use of an aqueous acidic extraction fluid.

It is therefore seen that the process of the invention is useful in connection with green coffee beans and decaffeination processes which would otherwise produce decaffeinated beans which then used to make

coffee beverage would result in a too-alkaline beverage. While particular embodiments have been described, variations will no doubt occur to those skilled in the art without departing from the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A method of tr ating gr en coffe beans comprising contacting green coffee beans with steam and an aqueous solution of an organic acid which is normally present in coffee beans, maintaining said green coffee beans in contact with said aqueous solution until a predetermined degree of acidification of said green coffee beans has occurred by absorption of said aqueous solution by said green coffee beans, said predetermined degree of acidification being that degree obtained by contacting said green coffee beans with an aqueous citric acid solution in a weight ratio of green coffee beans to citric acid solution of about 3/1 and allowing said citric acid solution to be fully absorbed by said green coffee beans, and wherein said citric acid solution has a citric acid concentration of between about 0.5% and about 3.5% by weight, and decaffeinating said acidified green coffee beans by extraction with supercritical carbon dioxide.

2. A method according to Claim 1, wherein said organic acid is selected from the group consisting of chlorogenic, tartaric, citric, and malic acids.

3. A method according to Claim 2, wherein said organic acid is citric acid.

4. A method according to Claim 1, wherein said predetermined degree of acidification is that obtained when said citric acid solution has a citric acid concentration of between about 1.0% and about 3.0% by weight.

5. A method according to Claim 4, wherein said predetermined degr f acidificati n is that

obtained when said citric acid solution has a citric acid concentration of between about 1.5% and about 2.0% by weight.

6. A method according to Claim 1, wherein said green coffee beans are maintained in contact with said aqueous acid solution until the moisture content of said green coffee beans is above about 20% by weight.

7. A method according to Claim 1, wherein said green coffee beans are maintained in contact with said aqueous acid solution until the moisture content of said green coffee beans is between about 25% and about 50% by weight.

8. A method according to Claim 1, wherein said green coffee beans are maintained in contact with said aqueous acid solution until the moisture content of said green coffee beans is between about 30% and about 35% by weight.

9. A method according to Claim 1, wherein said maintaining step comprises circulating said aqueous acid solution over said green coffee beans until said aqueous acid solution is substantially fully absorbed by said green coffee beans.

10. A method according to Claim 1, wherein said maintaining step comprises circulating said aqueous acid solution over said green coffee beans until the acid concentration in said beans is substantially the same as that in said solution.

11. A method according to Claim 1, wherein said contacting and maintaining steps are performed at between about room temperatur and about 80°C.

12. A method according to Claim 1, wherein said green coffee b ans are furth r proc ssed into final coff e product, and said final coffee product is adapted to produce a coffee beverage having an acceptable acidic character to its flavor.

13. A method according to Claim 1, wherein said green coffee beans are thereafter subjected to a roasting step.

14. A method according to Claim 13, wherein said roast coffee beans are thereafter processed into final coffee product.

15. A method according to Claim 1, wherein said steps of contacting with said aqueous solution and contacting with steam are performed simultaneously.

16. A method according to Claim 15, wherein said contacting steps are performed by placing said green coffee beans in a vessel, introducing steam into said vessel through an inlet adjacent to the bottom of said vessel, and contacting said green coffee beans with a spray of said aqueous acid solution from a spray head adjacent to the top of said vessel.

17. A method according to Claim 1, wherein said supercritical carbon dioxide comprises a mixture of carbon dioxide and water.

18. A method according to Claim 1, wherein said supercritical carbon dioxide has a pressure in excess of about 200 bar.

19. A method according to Claim 1, wherein said supercritical carbon di xid has a pr ssure in excess of 240 bar.

20. A method according to Claim 1, wherein said supercritical carbon dioxide has a pressure between about 250 bar and 310 bar.

21. A method according to Claim 1, wherein said supercritical carbon dioxide has a temperature between about 60°C. and about 120°C.

22. A method according to Claim 1, wherein said supercritical carbon dioxide has a temperature between about 70°C. and about 110°C.

23. A method according to Claim 1, wherein said extracting step is performed with a weight ratio of supercritical carbon dioxide to green coffee beans of between about 50/1 and about 300/1.

24. A method according to Claim 23, wherein said weight ratio is between about 75/1 and about 275/1.